Microstructure and Hardness of Copper Based Shape Memory Alloys with Fourth Alloying Elements

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ABSTRACT

Many potential applications of Cu based shape memory alloys (SMAs) are restricted due to the brittleness of the material. This research was conducted to enhance the mechanical properties of the Cu based SMAs. The research examined the effects of adding the fourth alloying elements, i.e., Boron (B), Cobalt (Co) and Titanium (Ti) on the microstructures and mechanical properties of the Cu based SMAs. The fabrication of Cu-Al-Ni alloys with these fourth alloying elements was carried out using a casting method. Several characterization tests were conducted to identify the effects of the fourth alloying elements using Scanning Electron Microscope (SEM), Optical Microscope, and Vickers hardness test. From the microstructural observation, it was found that the grain sizes of these alloys were refined with the addition of the fourth alloying elements. The addition of B shows the most fined grain size. The SEM results indicate that the microstructures consisted of two types of martensite, which were $\beta_1$with an 18R structure, and γ_1 with a 2H structure. The γ_1, looking like parallel martensite morphologies, are known as lamella structures. This type of lamella morphologies has also grown into grain. The β_1 phase is typically formed with self accommodating groups in two different morphologies, plates and needles. The precipitation existed in the structure known as γ_2, which also existed and acted like barriers in the grain boundaries. γ_2 precipitates can be found in grain boundaries and in between structure β_1 and γ_1. The addition of the fourth alloying elements shows an increment in the hardness of the alloys in which the addition of Ti element demonstrates the highest hardness value.

Keywords: *Shape memory alloys, Cu based shape memory alloys, fourth alloying elements, microstructure, hardness*

1.0 INTRODUCTION

Cu-Al-Ni SMAs have been developed for high-temperature engineering components such as sensors and actuators. This is due to their ability to work at temperatures near 200°C, which is better than other SMAs such as NiTi and Cu-Zn-Al alloys. These alloys are able to work at temperatures of just around 100°C. Cu-Al-Ni SMAs are much cheaper and do not require any complicated processing during manufacturing compared to NiTi/Cu-Zn-Al SMAs. As a result, these alloys have been widely used. Besides, they have a small hysteresis and high transformation temperatures compared to other alloys.

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Despite all of these advantages, these alloys have limitations such as brittleness and low phase recovery strains and stress. The compositions of Cu-Al-Ni are highly important as the shape memory effect can be found within 11-14% wt aluminum and 3-5% wt nickel only [1]. Also, different compositions for aluminum and nickel affect the properties and the transformation temperatures of the alloys. A higher percentage of aluminum can lead to the formation of precipitation of γ_2 [2]. The increasing of nickel content will also make the alloys become brittle. Therefore, the optimum composition needs to be investigated based on their specific applications.

Many potential applications are restricted due to the brittleness of polycrystalline Cu based SMAs [3]. In fact, polycrystalline alloys normally suffer from intergranular failure which might be due to the presence of γ_2 phase at grain boundaries [4]. Adding alloying elements is one of the methods to improve the properties of Cu-Al-Ni SMAs [5]. Studies have found that adding the fourth elements on Cu-Al-Ni SMAs such as manganese, (Mn), boron (B) and zirconium (Zr) can reduce the grain size, which in turn may improve the ductility of the alloys [6]. Ti also possesses grain refinement. It dissolves and is formed in grain boundaries which restricts the grain growth [7]. The addition of the alloying elements shows a significant effect on the mechanical properties. The objective of this study is to investigate the effects of addition of the fourth elements in Cu-Al-Ni -X SMAs, on their microstructures and hardness value.

2.0 METHODOLOGY

Cu-13 wt.%Al-3.5 wt.%Ni with different weight % of Co, Ti, and B were produced by melting the pure metals of Cu (99.999%), Al (99.999%), Ni(99.95%), Co(99.95%), Ti(99.95%) and B(99.95%) in a silicon carbide crucible at a temperature of 1300 ºC. Table 1 shows the alloy composition for each of the specimens. The ingots were homogenized at 900°C for 30 mins and then quenched in water in order to form martensite. The cast ingots were cut into pieces for characterizations and mechanical tests. The microstructures were observed using optical microscopy (OM) and Scanning Electron Microscopy (SEM). In order to investigate the microstructures of the alloys, the quenched specimens were ground with different grit size SiC papers in the following order of 200, 500 and 1000, polished, and etched in a solution of 10 ml HCl, 2.5 g ferric chloride acid ($FeCl_3.6H_2O$) and 48 ml methanol (CH_3OH). The hardness of the specimens was measured using *Vicker's* hardness test with 10 kg for 25 s.

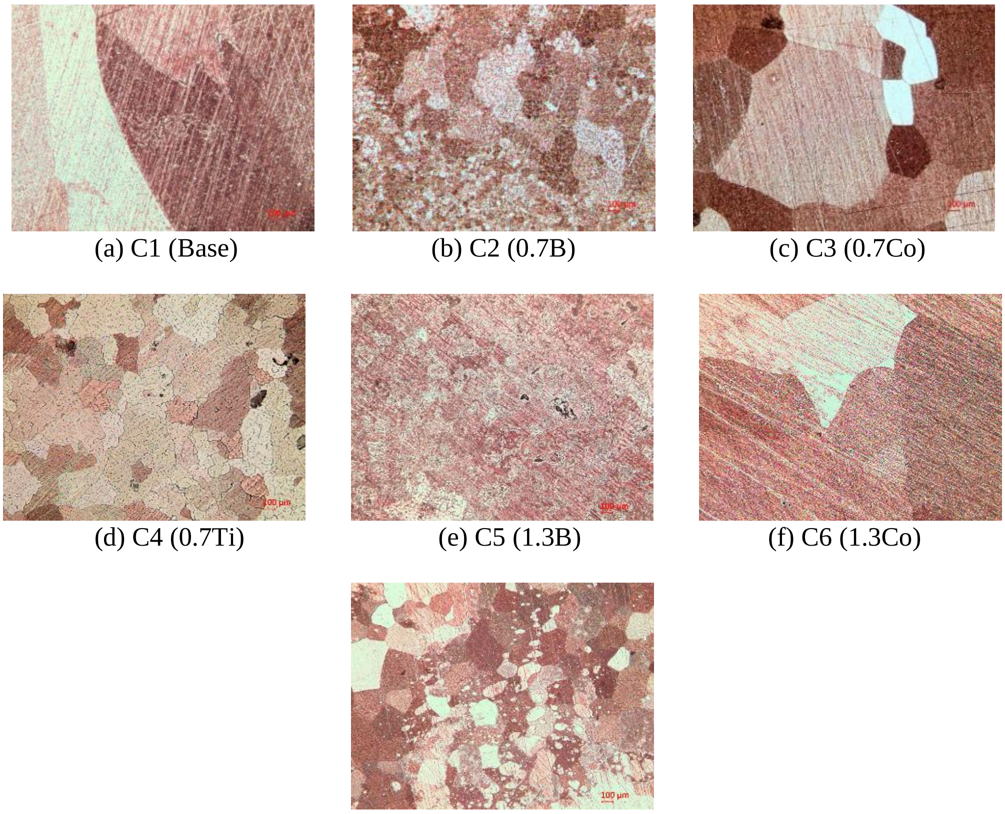
Table 1: Alloy composition (wt%)

Alloy	Cu	Al	Ni	B	Co	Ti
C1	83.5	13	3.5	-	-	-
C2	82.8	13	3.5	0.7	-	-
C3	82.8	13	3.5	-	0.7	-
C4	82.8	13	3.5	-	-	0.7
C5	82.2	13	3.5	1.3	-	-
C6	82.2	13	3.5	-	1.3	-
C7	82.2	13	3.5	-	-	1.3

3.0 RESULTS AND DISCUSSION

3.1 Microstructural Observation

The microstructure observations of the Cu-Al-Ni SMAs with the addition of B, Co and Ti are presented in Figures 1 and 2. Figure 1 shows the optical micrograph for each of the specimens, whereas Figure 2 shows the SEM micrographs. The grain sizes of the specimens are shown in Figure 1, whereas the martensite morphology and precipitation formations for different alloys are shown in Figure 2. Two different types of martensite could be observed, namely the self-accommodating zig-zag morphology groups of β_1' martensite and the course variants γ_1' martensite [8]. The $\beta`_1$ phase was formed in small needles with self-accommodating zig-zag morphology in between the thick plates of the $\gamma`_1$ martensite phase. By comparing the optical micrograph in Figure 1, it can be clearly seen that the grain size of C2 was reduced with boron addition compared to the base alloy C1 without addition. By increasing the percentage of boron, the grain size of C5 with higher boron content became even smaller than C2 with lower boron content.



(a) C1 (Base) (b) C2 (0.7B) (c) C3 (0.7Co)

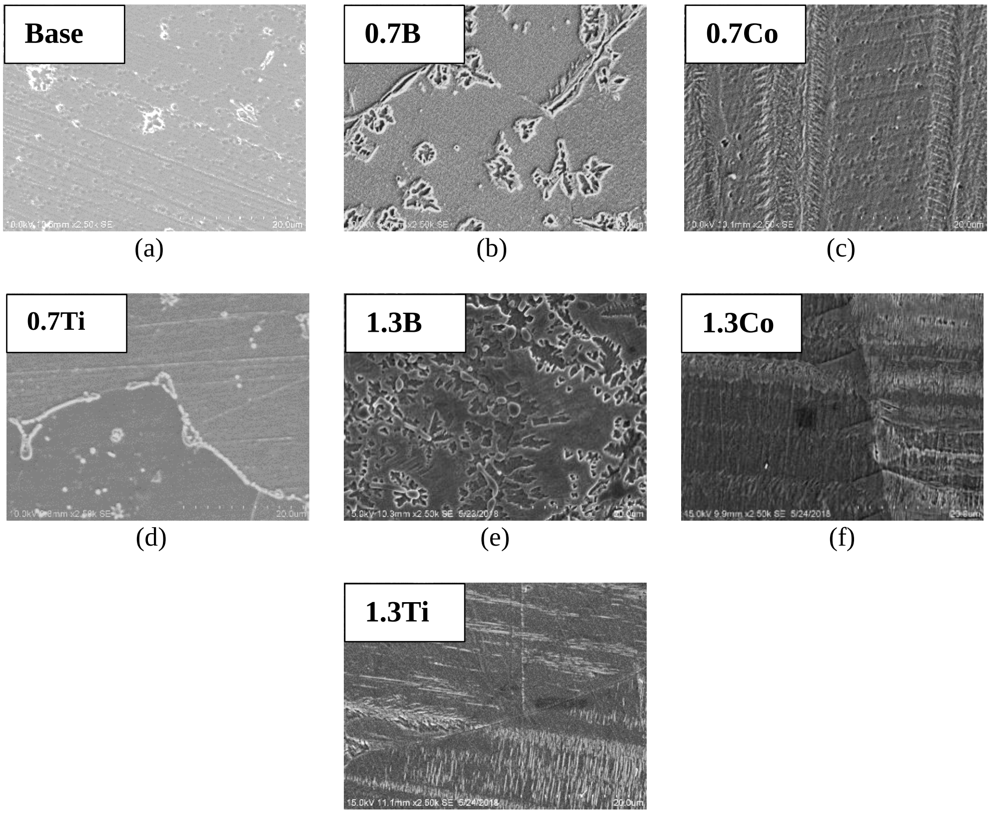
(d) C4 (0.7Ti) (e) C5 (1.3B) (f) C6 (1.3Co)

(g) C7 (1.3Ti)

Figure 1: Optical micrographs of Cu-Al-Ni SMAs

This might help to improve the mechanical properties since the boron restricted the grain growth. The SEM microstructures of boron additions are precipitation formation on the SEM micrographs for C2 and C5 (Figure 2). Compared to the boron addition in Figures 2(b) and (e) with the base alloy C1, a new precipitation formation was diffused into the grain boundary [6]. With the addition of Co, the morphology of $\beta`_1$ and $\gamma`_1$ martensite varies according to the percentage of the addition, in which the thickness of $\gamma`_1$ plate increases with increasing volume fraction of $\beta`_1$ phase. On the other hand, some intermetallic compounds/precipitations coexisted in the microstructure of the Cu-Al-Ni SMA after the addition of Co [9]. For the addition of the alloying element Ti, the grain size is also reduced, as shown in Figures 1(d) and (g) compared to C1 of Figure 1(a). This reduction is attributed to the formation of precipitates that abstain the nucleation and grain growth by the pinning effect [10]. This shows that the addition of Ti contributes to grain size refinement. Figure 2 demonstrates that the martensite phase can be seen in all the microstructures in different morphologies. Figures 2(d) and (g) show that many precipitations are formed, which consist of the addition of the fourth elements 0.7 wt% Ti and 1.3 wt% Ti, respectively. As reported by Tadaki, the martensite phase is disordered

18R (β_1') for 11-13 wt% Al and 2H(γ_1') for more than 13 wt% Al [2]. Therefore, both martensite phases are considered to be present. Furthermore, as can be seen in Figures 2(d) and (g), there are many precipitations found in the microstructures, which accumulate at the grain boundaries and they restrict grain growth. From the literature review, the addition of the fourth elements to Cu-Al-Ni tends to form intermetallic compounds with Al and Ni. Therefore, with the addition of the fourth elements B, Co and Ti, new precipitations were formed in different shapes and distribution of these precipitates between γ_1' and β_1' phases.



(g)

Figure 2: SEM micrographs of Cu-Al-Ni alloys with 2.5k × magnification: (a) C1 (b) C2 (c) C3 (d) C4 (e) C5 (f) C6 and (g) C7

3.2 Microhardness

Tables 2 and 3 show the results of the hardness of Cu-Al-Ni SMAs with and without the addition of alloying elements. The addition of the fourth elements contributes to grain growth refinement which significantly influences the mechanical properties of Cu-Al-Ni SMAs. Also, the precipitation formation on the microstructure also plays an important role in the mechanical properties.

It can be seen that the addition of alloying elements significantly increased the hardness value. This is due to the precipitation formation in the microstructure which restricted the movement of dislocation. It is found that the highest hardness value in 0.7 wt% addition of alloying elements is 0.7 wt% of Ti with 336.9 Hv. In addition, it was found that the highest hardness value among 1.3 wt % of alloying elements is 1.3 wt% Ti with 371.9 Hv. With the reduction of grain size, the hardness is increased. It can be seen that by adding the fourth alloying elements, it leads to the enhancement of the hardness value due to the presence of the participates in the microstructure, restricting the movement of dislocations and martensite variant interfaces [6] and increasing the microhardness.

Table 2: Hardness of the Cu-Al-Ni alloys (0.7% alloy elements)

Alloy	C1	C2	C3	C4
Hardness (Hv)	240.3	257.2	313.5	353.9
	215.7	289.9	296.5	300.9
	213.2	272.5	304.5	355.9
Average	223.1	273.2	304.8	336.9

Table 3: Hardness of the Cu-Al-Ni alloys (1.3% alloy elements)

Alloys	C1	C5	C6	C7
Hardness (Hv)	240.3	340.7	328.8	309.9
	215.7	309.9	335.5	393.1
	213.2	324.6	330.4	412.6
Average	223.1	325.1	331.6	371.9

4.0 CONCLUSION

The grain size of Cu-Al-Ni SMAs was reduced with the addition of the fourth alloying elements, B, Co and Ti. The addition of 0.7 wt% B followed by the addition of 0.7 wt % Ti and 0.7 wt% Co was found to produce the most fined grain size. The addition of 1.3%B is the finest grain size among these alloys. This is due to the presence of precipitation formation which restricted the grain growth, and this might enhance the mechanical properties. For the SEM result, it was hard to observe and differentiate the microstructure based on recent studies that show that the microstructure consisted of two types of martensite, which were $\beta_1$with an 18R structure and γ_1 with a 2H structure. The γ_1, looking like parallel martensite morphologies, are known as lamella structures. This type of lamella morphologies has also grown into the grain, while the β_1 phase is typically formed with self-accommodating groups in two different morphologies which are the plates and needles. The highest level of hardness among the alloys with 1.3 wt% Ti addition. Further research is suggested to investigate their mechanical properties and the shape memory recovery of these alloys.

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REFERENCES

1. Otsuka K. and Wayman C.M., 1999. *Shape Memory Materials*, New York, Cambridge University Press.
2. Tadaki T., 2002. Cu Based Shape Memory Alloys, *Shape Memory Materials*, Cambridge: Cambridge University Press.
3. Lojen G., Gojić M. and Anžel I., 2013. Continuously Cast Cu–Al–Ni Shape Memory Alloy – Properties in As-cast Condition, *Journal of Alloys and Compounds*, 580: p. 497-505.
4. Miyazaki S., Kawai T. and Otsuka K., 1982. On The Origin of Intergranular Fracture in β Phase Shape Memory Alloys, *Scripta Metallurgica*, 16(4): 431-436.
5. Saud S.N., Hamzah E., Abu Bakar T.A., Hosseinian S.R., 2013. A Review on Influence of Alloying Elements on the Microstructure and Mechanical Properties of Cu-Al-Ni, *Jurnal Teknologi,* 64: 51-56.
6. Morris M.A., 1991. Influence of Boron Additions on Ductility and Microstructure of Shape Memory Cu-Al-Ni Alloys, *Scripta Metallurgica et Materialia*, 25(11): 2541-2546.

7. Hurtado, I., Ratchev P., Van Humbeeck J., Delaey L., 1996. A Fundamental Study of The χ-phase Precipitation in Cu-Al-Ni-Ti-(Mn) Shape Memory Alloys, *Acta Materialia*, 44(8): 3299-3306.
8. Sarı U. and Aksoy İ., 2006. Electron Microscopy Study of 2H and 18R Martensites in Cu–11.92 wt% Al–3.78 wt% Ni Shape Memory Alloy, *Journal of Alloys and Compounds*, 417(1–2): 138-142.
9. Wee Y.C., Abubakar T., Hamzah E., Saud S., 2015. Phase Transformation and Microstructure Behaviour of Cu-Al-Ni Shape Memory Alloys Incorporated with Cobalt Addition, *Jurnal Teknologi*, 74: 53-56.
10. Sure G.N. and Brown L.C., 1985. The Fatigue Properties of Grain Refined β-Cu Al Ni Strain-Memory Alloys, *Scripta Metallurgica*, 19(4): 401-404.